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QUASI-LIQUID CRYSTALLINE MATERIALS
WITH SPECIAL ELECTRO-OPTIC PROPERTIES

Final Technical Report

by

Valeri Krongauz

December 1988

United States Army

European Research Office of the US Army

London, England

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ABSTRACT

Photo/thermochromic liquid crystals and liquid crystal polymers were synthesized by combination of spiropyran and mesogenic groups in one low molar mass molecule or macromolecule. The spiropyran-merocyanine conversion affects the mesophase structure and results in formation of non-centrosymmetric non-linear optical material, generating second harmonics. Aggregation of merocyanine molecules leads to a new photomechanical effect in low molar mass compounds and to the rheo-optical and boundary spectral effects in the side chain liquid crystal copolymers containing spiropyran side groups. Polychronic phototransformations in the copolymers as well as accompanying structural changes enable use of the polymer films for optical information storage.



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Side chain liquid crystal polymers

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Spiropyrans

Thermochromism

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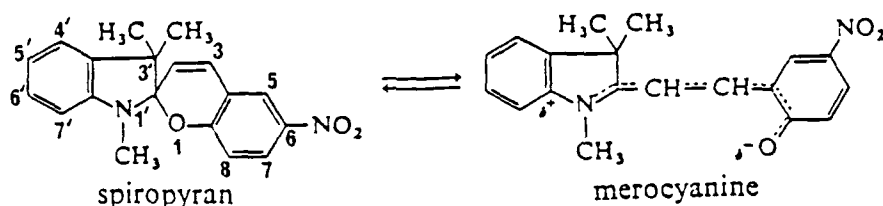
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Objective and Significance of the Research

Spiropyrans are the most important organic photo- and thermo-chromic molecules [1]. They can be reversible converted to a merocyanine dye by u.v. irradiation or heating:

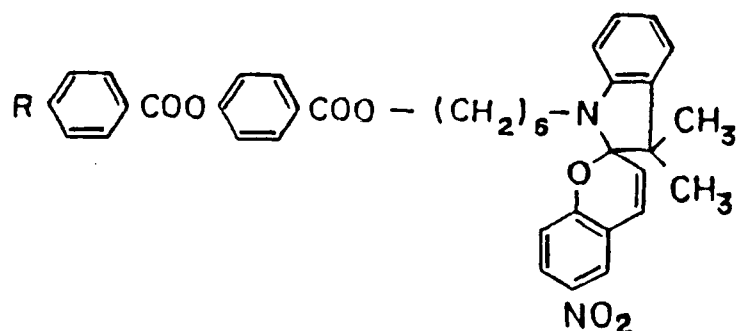


Since this transformation leads to drastic changes in such molecular properties as polarity, tendency to aggregate, molecular geometry, etc., we anticipated that the combination of spiropyrans and mesogenic groups in a single molecular structure should lead to novel types of molecular organizations with new interesting properties.

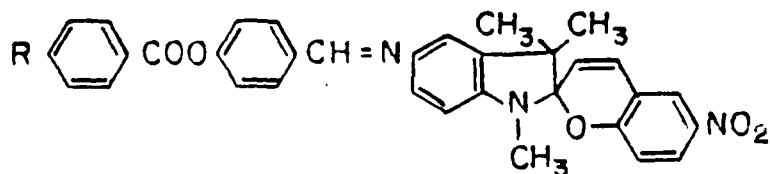
Indeed, there was good reason to believe that such "hybrid" molecules should show not only photo- and thermo-chromic mesophases but that many of the physical properties could be manipulated by heating and light. In particular the transformation of the molecules into the merocyanine form by heat or irradiation and their alignment in an electrostatic field would allow us to obtain a dipolar non-centrosymmetric structure with high optical non-linearity.

Our efforts in this direction include the synthesis of both low molecular weight molecules and macromolecules containing spiropyrans and mesogenic groups.

The initial experiments with low molar mass compounds showed that the combination of photo/thermochromic and mesogenic moieties in one molecule often led to impairment of one of the properties. Which one of the properties was lost depended markedly on the position and type of the "bridge" by which the mesogenic group was connected to the spiropyran molecule. The T-shaped molecules of the general formula



showed good photo- and thermo-chromic behaviour but do not exhibit mesomorphic properties. However, in the melt of one of them, that with $R = CN-$, we discovered a very unusual and intriguing photocontraction effect [2]. This melt, produced by the irradiation and heating of amorphous films of the material, contracts markedly under u.v. irradiation. The unprecedented character and importance of such effect was emphasized in a review of this work published in Chemical and Engineering News [3].



The rod-like "hybrid" molecules, on the other hand, displayed very special thermodynamic and structural properties resulting in the appearance of a new kind of molecular organization [4, 5].

The latter compounds can be crystallized from solution and give crystals with sharp melting points and crystal-isotropic liquid phase transition. However, under certain conditions the compounds form amorphous metastable films that exhibit a characteristic birefringent texture upon heating. Appearance of this texture coincides with a sharp increase of merocyanine concentration due to the thermochromic spiropyran-merocyanine conversion.

Further increase in temperature leads to disappearance of this texture. The temperature range of the birefringent texture is wide (80° - 90°) and lies much below the melting point of the crystals. Since these materials show some features of liquid crystals, but behave differently from conventional mesophases, we named them Quas-liquid Crystals (QLC's).

Substantial efforts were made to determine the structure of these materials which proved to be a nematic-like mesophase with a structure that is strongly affected by the presence of the highly dipolar merocyanine groups [5-7].

QLCs can be aligned in an electrostatic field of more than 0.5 kV/mm. The electric field induced orientation of the films stabilizes the quasi-liquid crystalline state (crystallization no longer occurs), to such an

extent that at room temperature the orientation and the glass like properties are preserved practically indefinitely [4, 5].

It was discovered that such oriented films generate second harmonics on irradiation with a laser beam [8]. The studies on second harmonic generation proved the unique character of QLC's.

Indeed, in contrast to conventional nematic liquid crystals, where polar ordering has never observed, in quasi-liquid crystals a polar ordering of molecules can be observed in external fields and can be modified in a manner predictable by a mean field theory.

We finally accomplished the synthesis of photochromic liquid crystals by preparing polyacrylate [9, 10] and polysiloxane [11] copolymers containing spiropyran and mesogenic side units. The culminating point in our studies of these materials was the observation that structural changes of the mesomorphic systems can be induced by the reversible spiropyran merocyanine photoconversion. As a result these liquid crystals form an exceptional class of optical materials in which many of the physical properties of the mesophase, such as birefringence, viscosity, etc. can be changed by light. The photoinduced aggregation of the merocyanine dyes, for example, leads to a network formation and new rheo-optical effect [9], observed above the clearing point. A very unusual spectrum broadening effect near a film edge was observed and interpreted by the existence of separate mesogenic and photochromic domains in the polymers [12].

Since these materials combine photosensitivity with the physical properties of liquid crystal polymer, they open innumerable possibilities for applications in optical technology. The possibility to control by light and temperature the formation of the three primary colors [11], for example, makes them interesting materials for new applications in display technology. Moreover, they can be used for the storage of optical information because, as was already mentioned changes in absorption and birefringence can be induced by light.

In this respect we have used these materials as a medium for the storage of digital intensity distributions. The merocyanine to spiropyran isomerization, which influences locally the liquid crystal orientation causes the optical induction of a birefringence pattern in a pre-oriented polymer liquid crystal film. This may result in the recording of information.

There are many scientific implications and potential applications for photo- and thermochromic liquid crystals. A measure of the promise of these materials is given in recent scientific reviews of our work in NATURE [13] and Chemical and Engineering News [14, 15].

COMPREHENSIVE DESCRIPTION OF THE PROJECT*

Monomeric Spiropyrans with Mesogenic Groups

* More detailed experimental data and discussions are given in our papers cited in the List of Publications.

The low molecular weight spiropyrans containing mesogenic groups are thenno- and photo-chromic in solution. Their crystals have sharp melting points and give green or greenish-blue isotropic melts. Thin amorphous films of the compounds can be obtained by casting from solution. These films are metastable and remain in the amorphous state from hours to days. We ascribe the formation of the amorphous films to the presence of merocyanine molecules, which apparently act as impurities, retarding the crystallization of the films. As is discussed below, the properties of the amorphous films depend markedly on the position of the mesogenic substituent.

1.1 Photocontraction of Liquid Spiropyran-merocyanine Films [3)]

This amorphous films of "T-shaped" spiropyrans with mesogenic side groups, contrary to the "rodlike" ones, do not exhibit mesophase properties: on heating they give isotropic melts of blue color like the melt form the crystals. However, if an amorphous film of spiropyran with R = CN- is irradiated during slow heating from room temperature to about 60°-70°, it acquires an uniform, stable cherry-red color.

The photocontraction effect occurs when this red fluid film is irradiated with intense u.v. light at temperatures in the range of 85°-150°C.. The net volume of the films is reduced by 10-20%, depending on the film thickness, light intensity and conditions of preparation. The thicker the film the less pronounced is the effect.

On subsequent standing in the dark the films expand again. The contraction and expansion lag after, respectively, the start and shut-off of the illumination. These lags in change of the film volume on illumination by chopped light at temperatures of 120°-130°C produce an effect which is reminiscent of the pulsation of unicellular organisms. However, after several such cycles the rate of contraction of a given film slows down, and eventually no volume changes are detected in finite times of observation.

Spectroscopic and X-ray examination of the material allowed us to suggest that the photocontraction is due to the stacking of the merocyanine molecules, formed on illumination, into H-aggregates. In essence the photocontraction arises from replacement of the van der Waals distances between bulky spiropyran molecules by the distances between merocyanines in closely packed molecular stacks. The stacks are not stable at high temperature, and the back merocyanine-spiropyran reaction proceeds in the dark. Apparently the mesogenic groups provide an arrangement in which head-to-head positioning of the spiropyran moieties facilitates formation of the merocyanine stacks.

1.2 The Quasi-liquid Crystal Structure [4-7]

The metastable amorphous films of the rod-shaped compounds give a birefringent texture upon heating. Appearance of such texture, characteristic of a mesophase, coincides with a sharp increase in the merocyanine concentration, resulting in a color change of the films from

yellow to green, due to thermochromic spiropyran-merocyanine conversion. Apparently the thermochromic conversion induces the phase transition to the mesophase. Further increase in temperature leads to the disappearance of texture but it appears again upon cooling. The temperature range of the birefringent texture is rather wide (for example, spiropyran with $R = CH_3O-$ has a texture between 50-130°C) and lies much below the melting point of the spiropyran crystals ($\sim 100^\circ C$). The mesophase is non monotropic.

The quasi-liquid crystalline films crystallize with time. The films can be aligned in an electrostatic field of more than 0.5 kV/mm. The alignment of the films stabilizes the quasi-liquid crystalline state and spontaneous crystallization no longer occurs. Under supercooled conditions at room temperature the mesophase with homogeneous alignment is preserved practically indefinitely.

Different methods usually employed for investigation of conventional liquid crystals were adapted for the studies of QLC films. We determined the polarization absorption and fluorescence spectra in the visible and u.v. regions of QLC's, pure and with different additives, and the polarization ESR spectra of a paramagnetic probe in the aligned films. FTIR spectroscopy was used for investigation of the polarization of different groups in the spiropyran molecules aligned in films. Differential scanning calorimeter measurements and microscopic studies were used for establishing the miscibility and phase diagrams of QLCs with conventional liquid crystals of a different nature.

The analysis of all these data allowed to suggest that [7]: The QLC phase represents an intrinsic two-component mesophase, with properties that are substantially determined by strong interactions between the molecules of these components. The benzopyran groups of spiropyran molecules, interacting with each other, create a site with some features of a smectic phase and at the same time distort the parallel arrangement of the molecules due to the non-planar attachment of the mesogenic rest of the molecules. The merocyanine molecules, on the other hand, improve the directional order of the spiropyran molecules in their environment and destroy smectic-like sites, promoting the nematic properties of the mesophase. Obviously the nematic and smectic-like sites are in a dynamic equilibrium which relates to the equilibrium between merocyanine and spiropyran molecules. The two component nature of the mesophase is also a major factor in stabilization of this metastable state which occurs much below the crystal melting point.

Remained answered, however, was the question whether the QLC state is centrosymmetric, as is the conventional nematic state, or non-centrosymmetric with a ferroelectric-type arrangement in an electrostatic field. Optical second harmonic generation [16] is an ideal tool for such study because, within the electric-dipole approximation, the second-order nonlinear process is forbidden in the centrosymmetric medium.

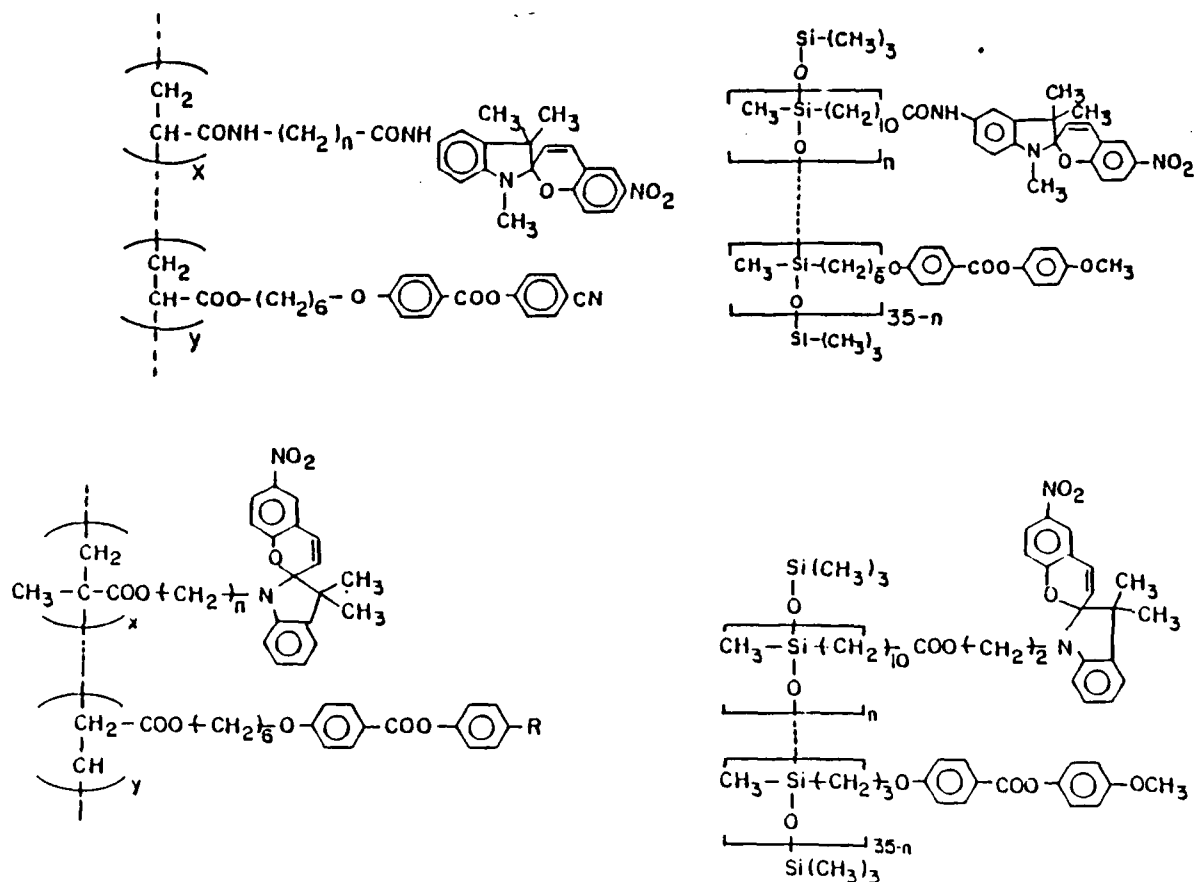
1.3 Non-Linear Optical Properties of QLCs [8]

A second harmonic generation (SHG) study of QLC films indicated that QLCs are non-centrosymmetric with a polar axis pointing along the director (i.e., the average molecular orientation) defined by the direction of the aligning electrostatic field during preparation. This symmetry should arise from a polar alignment of the molecular dipole moments. The polar ordering of molecules can be modified by an external electrostatic field along the director, as manifested by an E-field dependence of the SHG.

Polar ordering has never been observed in conventional liquid crystals in the nematic state; that is, molecules tend to have equal probabilities pointing in opposite directions along the director. Local anti-ferroelectric pairing of molecules is also known to exist in many liquid crystals consisting of strong polar molecules. This is due to the tendency of nearby dipoles to be anti-parallel to each other in order to reduce their repulsive dipole-dipole interactions [17]. In QLCs, however, merocyanine molecules are separated by a few spiropyrans which could screen the dipole-dipole interactions among merocyanines and allow a preferred polar alignment of these molecules. The spiropyrans themselves could also have a polar ordering with an axis presumably pointing opposite to that of the merocyanines.

Photo- and Thermo-Chromic Liquid Crystal Polymers

The initial studies were conducted on polymers with spiroopyran side groups which did not contain mesogenic side chains (18,19). The results indicated that the aggregation of merocyanine moieties is so efficient that it proceeds even in dilute solution or in copolymers of spiroopyran monomers with such monomers as MMA. This aggregation leads to crosslinking of macromolecules and even to intramolecular stack formation by the merocyanine groups. Similar crosslinking processes were later observed in liquid crystal polyacrylate and polysiloxane copolymers with spiroopyran monomers [9, 11].



Liquid crystal polyacrylates were prepared by copolymerization of vinyl monomers with spiropyran and p-cyano-phenylbenzoate groups [10]. The liquid crystal polysiloxanes were obtained via active ester-mesogenic copolymers which were prepared by addition of mesogenic and hydroxysuccinimide-ester olefines to Si-H containing polymers [11].

Observation with polarization microscope revealed that the clearing points of the copolymers are lower the higher the content of spiropyran units in the copolymer.

2.1 Photo- and Thermo-Chromic Behaviour [9-11]

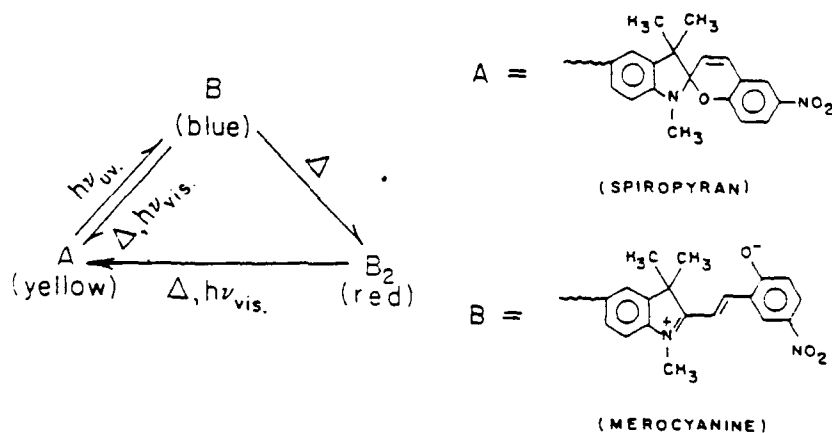
The photochromic behaviour of the copolymers depends strongly on the physical state of the materials (glassy, mesomorphic, isotropic) and the spiropyran-merocyanine equilibrium which exists at a given temperature.

In the fluid state, the copolymer films acquire a pink color due to the thermally formed merocyanine molecules. Irradiation of such a film with visible light brings about a pale yellow color ($\lambda_{\text{max}} \sim 370\text{nm}$), which corresponds to the spiropyran absorption. If the yellow film is irradiated with u.v. light at temperatures at which the side chains are immobilized the characteristic blue color ($\lambda_{\text{max}} 580\text{nm}$) of isolated merocyanine molecules is observed. For the polysiloxane copolymers, for examples, this occurs at temperatures below -10°C . If the u.v. irradiation of a yellow film is performed at temperatures around and above the glass transition, physical crosslinking of the macromolecules occurs due to aggregation of

the dye moieties. This is accompanied by appearance of a red color (λ_{\max} 550nm). The network formation is responsible for the appearance of a new rheo-optical effect described in part 2.2.

The yellow color can be restored by irradiation of blue or red films with visible light, i.e., the photoinduced crosslinking of the macromolecules is reversible.

The mechanism for these transformations is summarized below:



The electronic absorption spectra of the copolymer films show an increase of the merocyanine's absorption with temperature rise. The transition from amorphous to liquid crystalline phase is accompanied by increasing aggregation of the merocyanine molecules in molecular stacks. The optical density does not change appreciably with temperature up to the clearing point. The transition from mesophase to isotropic phase coincides with an increase of non-aggregated merocyanine molecules. Probably, above the clearing point, formation of the network is completed and restricted segmental mobility hinders further merocyanine association.

2.2 Rheo-optical Properties

A very remarkable feature of the isotropic films formed above the clearing point by the copolymers is very strong transient translucence between cross polarizers when they are squeezed between two glass slides or even lightly touched with the tip of a spatula

The liquid crystal homopolymers which do not contain spiropyran, do not exhibit this effect.

Usually such instant birefringence during mechanical disturbance is considered as an indication of homeotropic (orthogonal to solid surface) orientation of mesogenic molecules [20]. Therefore, one could conclude that instead of nematic-isotropic transition at the clearing point we observe a transformation of orientation of mesogenic groups of macromolecules from parallel to perpendicular to the surface.

To check this we treated the glass surface with cremophor [21] and nylon [22] which promote the planar orientation of liquid crystals and with 1-dodecanol [18] for the homeotropic alignment. We found no effect of the surface on the "sparkling phenomenon". A decisive experiment was performed with droplets of the copolymers, in an isotropic phase, connected with a surface through a relatively small area. For these droplets again even a very gentle touch gave remarkable sparkling, though in this case the effect of the surface must be insignificant. This suggests that the transient brightening is caused by at least partial restoration of liquid crystalline order, induced by mechanical disturbance.

The DSC measurements give endothermic peaks at temperatures that coincide with the microscopic observation of the clearing points. This confirms that the static birefringence disappearance relates to the mesophase-isotropic phase transition.

The rheo-optical properties of the copolymer films as a function of temperature were investigated with a parallel-disk type rheometer with transparent glass disks [9, 10]. The results revealed that introduction of relatively small portion of the spiropyran groups causes a drastic increase in the viscosity of the polymers. This indicates that the interaction of the merocyanine groups, formed on heating or irradiation, gives rise to the aggregation of macromolecules in a network with high viscosity.

The formation of such a network by physical crosslinking of the macromolecules due to dimerization of the merocyanine side groups is responsible for the appearance of the strong dynamic birefringence above the clearing point.

Presumably, the more rigid structure of the network favors the preservation by macromolecules of the conformation acquired in the mesophase even above the clearing point. This makes the dynamic ordering easier.

2.4 Anomalous photochromic phenomena observed near a film rim [12]

An interesting peculiarity of the photochromism of the copolymers in the glassy state was observed near the film rim. The visible absorption

band starts to grow broader on uv-irradiation when it was reaching the maximum absorption at λ_{max} . The effect of the spectrum broadening near the film rim was observed on all liquid crystal copolymers containing spiropyran groups, and even on a homopolymer containing spiropyran as a solute. The effect was most pronounced for the copolymers with T-shaped spiropyrans. For these copolymers the broadening was so strong that the peak was turned to a plateau, which looked like a superposition of at least three absorption bands. The short wavelength absorption band of the photochromic groups (around $\sim 380\text{nm}$) showed a bathochromic expansion at the rim, but the change was much less significant than the visible band.

The decoloration reaction proceeds on irradiation with visible light ($\lambda > 500\text{nm}$) in the reverse sequence: first the band becomes sharper and afterward the peak intensity of the band goes down. The same sequence of decoloration steps occurs also on heating the sample.

The scope of the facts related to the spectrum broadening near the film edge indicates that two conditions essential for the broadening: liquid crystalline structure and closeness to the film edge.

In order to explain our effect, we assume that the photochrome dye molecules are distributed non-uniformly in the polymer matrix and the dye concentration in a domain of mesogenic groups is probably reduced due to the structural incompatibility. Hardening of a polymer melt brings about defect formation in mesogenic domains. Defects were clearly seen at the edge of a film. It is conceivable that smaller defects are also formed at

the edge in larger proportions than in the middle. We may assume that the dye molecules are present at higher concentrations in the defective than in the more ordered mesomorphic regions and it is apparently spiropyrans entrapped near defects which give rise to the effect. Presumably the dye aggregation and interaction between dye molecule and a surrounding liquid crystal domain leads to the broadening effect. Apparently the interactions are strong enough to produce electronic level splitting, especially if one takes into account that merocyanine dyes have extremely high electronic polarizabilities. There is also a possibility of stronger aggregation of merocyanine groups in the defects near the boundary.

2.3 Electro-optic Storage Effects (Preliminary Results)

Side chains polymer liquid crystals (PLC) have been used to store optical data by a local optical heating of a preoriented PLC film into the isotropic phase. The resulting macroscopically unoriented light scattering spots are frozen-in by subsequent cooling. This technique has been called thermo-recording [23, 24].

Thermo-recording has serious drawback because the phase transition required for the writing of information is caused by the transformation of light into heat. This technique needs, therefore, the accumulation of a relatively large influx of energy during a very short time, i.e., high intensity of irradiation. Moreover, the diffusion of heat from the site of direct illumination diminishes the sharpness of the image.

The photochromic character of our materials allowed us to use a completely different method for optical recording. This new method is based on the reversible merocyanine-spiropyran isomerization which induces local director field distortions in a preoriented sample. As a result of such local disorientation a phase object appears due to spatial modulation of the refractive index. This way of recording does not need high intensity of irradiation and in addition the "instantaneous" nature of the initial photochemical act, less than 10^{-12} sec, makes the speed of recording very high. This is feasible because the reorientation, which proceeds with some lag, can be considered as a development.

For our preliminary experiments a photochromic polyacrylate copolymer containing p-cyano-phenylbenzoate moieties was used. In this polymer the dielectric anisotropy is strongly positive due to the cyano dipoles linked to the mesogenic units. This offered the possibility of orienting the polymer with the director parallel to an externally applied electric field.

The polymer films were prepared between two conducting glass plates that were separated by a 12 μ m spacer. A uniform homeotropic orientation was achieved by applying an appropriate electric field at temperatures just below the clearing point of the polymer. A completely clear monodomain film was obtained.

The storage was performed at room temperature employing linearly polarized green light ($\lambda = 514\text{nm}$), which is absorbed by the merocyanine molecules. Optically induced molecular reorientation allowed one to recognize the stored information in the polarizing microscope.

The erasure of the stored information was achieved by heating the film to temperatures above the clearing point. Although these results clearly proved the potential of these materials as storage medium for optical recording the rigidity of the polyacrylate backbone is a disadvantage because the reorientation process is dominated by the polymer viscosity [25]. With this in mind and since we already know how to synthesize photochromic liquid crystal polysiloxanes a series of cyano-containing polysiloxanes were prepared.

As was expected the more flexible polysiloxane backbone greatly improved the viscoelastic properties which are required for the electro-optic storage effects and the use of these polymers for holographic recording suggests a fruitful research area.

CONCLUSION

The superposition of an additional molecular arrangement, due to the merocyanine interactions, on the self assembling property of mesogenic molecules has been realized by the synthesis of low molar mass molecules and polymers containing spiropyran and mesogenic groups.

This superposition was "engineered" in the low molecular weight compounds by preparing two geometrically different types of molecules: in the T-shaped molecules steric factor is overcome by the dipole-dipole interaction of the merocyanine molecules resulting in photoactive but not mesomorphic materials. The photocontraction effect, however, which is

observed in one of these compounds, is dependent on the presence of the mesogenic group. This clearly points to the importance of this moiety though there is not a mesophase. In the rod-shaped molecules on the other hand, the geometrical anisotropy favors the mesomorphic properties and therefore the materials give a metastable mesophase: quasi-liquid crystals. This mesophase, however, is not a conventional liquid crystal in the nematic state because in this case the amorphous to mesophase transition is connected with a thermochromic transformations and the spiropyran-merocyanine interactions lead to a non-centrosymmetric mesophase with a polar axis pointing along the director. The unique structural characteristics of QLCs provide the opportunity to prepare ultra-thin organic films with non-linear optical properties for integrated optics and microelectronics.

With the synthesis of copolymers containing spiropyran and mesogenic side groups we finally obtained photochromic mesophases. The culminating point of our studies, however, was the observation that structural changes of the mesomorphic systems can be induced by the reversible spiropyran-merocyanine dye photoconversion. At temperatures at which the segmental mobility is limited, u.v. irradiation of the copolymers results in formation of isolated merocyanine molecules. At higher temperatures aggregation of the dye moieties takes place leading to network formation and a new rheo-optical effect, observed above the clearing point. The spectrum broadening effect indicates the space separation of photochromic and mesogenic side chains. The reverse photoconversion of merocyanine to spiropyran occurs on irradiation with visible light.

We have already proved the use of these materials as storage medium for optical information. The possibility of altering the mesophase by light opens a way to many other scientific and practical applications including specialized optical elements, waveguides, non-linear materials for optical computing systems etc. We therefore, hope that the scientific interest in photochromic liquid crystals will increase.

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